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COMMITTEE OF EXPERTS ON THE
TRANSPORT OF DANGEROUS GOODS

Sub-Committee of Experts on the
Transport of Dangerous Goods
(Fifteenth session,
Geneva, 29 June-10 July 1998,
agenda item 5 (a))

# MISCELLANEOUS DRAFT AMENDMENTS TO THE MODEL REGULATIONS ON THE TRANSPORT OF DANGEROUS GOODS

## Other draft amendments

## Listing and classification
## Lithium batteries

Transmitted by the experts from France, Germany and the United States of America

## Introduction

1. The Expert from the United States submitted a document to the fourteenth session of the Sub-Committee that proposed various amendments to the provisions for the transport of lithium batteries (see document ST/SG/AC.10/C.3/1997/83). These proposals were intended to take account of advancements experienced in the development of new lithium battery technologies, as well as increases in the size of lithium batteries now being produced for various applications, including for purposes of electric vehicle propulsion. Owing to lack of time, the Sub-Committee was not able to consider these proposals. However, detailed written comments on the proposals were provided to the expert from the United States by the experts from France and Germany. This document presents revised proposals that take into account the written comments offered on document ST/SG/AC.10/C.3/1997/83, as well as the results of subsequent informal discussions between the experts from France, Germany and the United States.

2. In general, the explanation of, and rationale for the changes proposed in document ST/SG/AC.10/C.3/1997/83 remain valid. Accordingly, those arguments are not reproduced in this document. The discussion section of this document only addresses new or additional issues not examined in the previous document, or issues where further explanation is considered necessary. However, to facilitate consideration of the specific amendments proposed, all of the amendments proposed in document ST/SG/AC.10/C.3/1997/83, modified, when appropriate, by the comments received, subsequent informal discussions between experts, and/or to improve clarity, are presented herein.

**Discussion of additional issues**

3. Aggregate Lithium Content.

3.1 Further clarification is considered appropriate with respect to the introduction of the term "lithium content", as proposed in document ST/SG/AC.10/C.3/1997/83. It was proposed that the 12 g per cell and 500 g per battery lithium or lithium alloy quantity limitations be removed from Special Provision 230, and be used only in the Manual of Tests and Criteria for purposes of determining the number and condition of cells and batteries to be tested. A note to this effect would be added to Special Provision 230. Moreover, owing to the fact that lithium can be present in a variety of forms (e.g., pure lithium metal, combined with chemically inert metals as metal alloys, or intercalated into chemically inert carbon or graphite hosts), it was further proposed that where the 12 g/cell and 500 g/battery mass limits would continue to appear in the Test Manual, these limits would apply to the aggregate "lithium content" of the negative electrodes and not to the aggregate mass of "lithium or lithium alloy" in cells or batteries (as it appears in the current Recommendations).

3.2 Use of this term allows the mass limitations to be applied on the basis of what may be viewed as an "equivalent" lithium content. That is, if lithium is alloyed or intercalated in an inert host, the mass limitation would not be applied to the mass of the alloy or host (of which only a fraction is lithium), but rather to the mass of lithium present in the alloy or host. It is considered appropriate to apply this concept in that the capacity of a cell or battery to store energy (and, therefore, its potential heat generating hazard in transport), is directly related to the quantity of lithium present, not to the mass of any alloy or inert host plus the lithium that may be contained therein. Thus, regardless of the form in which the lithium is present (pure, alloyed, or intercalated in an inert host), the mass limitations would be applied on the basis of the equivalence to pure lithium. The actual aggregate anode lithium content of a battery is the anode lithium content of the cell multiplied by the number of cells in the battery.

3.3 As a consequence of the introduction of this concept into the Test Manual, similar terminology should be employed in the text of Special Provision 188 (in which mass limitations are also specified in terms of mass of "lithium or lithium alloy"). However, this consequential change had not been proposed in document ST/SG/AC.10/C.3/1997/83. Appropriate amendments in this regard are proposed in a separate document.

4. Expression of cell and battery lithium content mass limitations in Test Manual.

4.1 As stated above, it was proposed in document ST/SG/AC.10/C.3/1997/83 that the 12g per cell and 500 g per battery limitations on lithium content that now appear in Special Provision 230 should instead appear only in the Manual of Tests and Criteria for purposes of specifying the number and condition of cells and batteries required to be tested. Thus, in effect these limitations would be used to distinguish between "large" and "small" cells and batteries for testing purposes. In the relevant amendments proposed to the Test Manual, expression of the testing distinctions between such "large" and "small" cells and batteries resulted in repetitive use of lengthy qualifying phrases such as "for cells in which the lithium content of the anode is not more than 12 g, and for batteries in which the aggregate lithium content of all cell anodes is not more than 500 g...." To avoid repetitive use of such qualifying phrases, and, thereby, improve the clarity and editorial presentation of the relevant test requirements, it is proposed herein to use the 12 g and 500 g limitations in appropriate definitions for "small" and "large" cells and batteries. For example, a "large cell" would be defined as a cell in which the lithium content of the anode is more than 12 g, and a "large battery" would be defined as a battery in which the aggregate lithium content of all cell anodes is more than 500 g. These definitions would appear only once in 38.3.3.2 of the Test Manual, with the text of the actual tests being simplified by using the defined terms "small cell", "small battery", "large cell" and "large battery", as appropriate.

5. Test T.1.

5.1 Comments on document ST/SG/AC.10/C.3/1997/83 suggested that a modification was necessary to the extreme temperature test provisions in Test T.1 to properly take account of the practical aspects of testing and shipping large cells and batteries. In this regard, it was noted that owing to the possible need for mechanical handling of very large batteries, the time period between storage at the high and low temperatures should be extended from 5 to 10 minutes. This comment has been incorporated into the proposed amendments to Test T.1.

6. Test T.2.

6.1 Comments on document ST/SG/AC.10/C.3/1997/83 suggested that certain modifications were necessary to the shock test provisions in Test T.2 to properly take account of the practical aspects of testing and shipping large cells and batteries. With regard to the shock test provisions, it was noted that the required peak acceleration currently specified (125 to 175 times the local acceleration of gravity ("g")) is not realistic for large cells and batteries in that the higher mass of such articles results in excessively large forces being applied in testing. It was suggested that for such cells and batteries, the peak acceleration required should be not less than 50 g, which must be achieved over a maximum duration of 11 milliseconds (as is provided in Table II of IEC Standard 68-2-27). These comments have been incorporated into the proposed amendments to Test T.2.

7. Test T.3.

7.1 Comments on document ST/SG/AC.10/C.3/1997/83 suggested that certain modifications were necessary to the shock and charge test provisions in Test T.3 to properly take account of the practical aspects of testing large cells and batteries. With regard to the shock test provisions, the same suggestions were made as were described above in relation to the shock test provisions of

Test T.2. With regard to the charge test, in order to exclude the need to take account of the current draw experienced during short-term power pulses it was proposed to clarify that the current draw required to be maintained is the maximum "continuous" current specified by the manufacturer. In addition, if in testing certain types of cells it is found impossible to achieve this level of current draw when employing the testing procedure prescribed in 38.3.4.3.3 (e.g., for cell technologies that are designed to operate most efficiently at temperatures well above the temperature at which the cells are tested or typically transported), it was suggested to limit the required current draw to the maximum attainable under the prescribed test procedure at the ambient temperature at which the test is performed. These comments have been incorporated into the proposed amendments to Test T.3.

8. Test T.4.

8.1. In document ST/SG/AC.10/C.3/1997/83, the expert from the United States drew the Sub-Committee's attention to certain deficiencies with the Test T.4 (internal short circuit) test procedure that have come to light in attempting to apply the procedure to the testing of large cells. Comments submitted supported the need for changes to the procedure for performing the T.4 test. Specifically, it was suggested that the diameter of the rod used to apply the "crushing" force should vary in proportion to the size of the cell tested, with the rod diameter being not less than 50% of the smallest cell overall dimension (or 6 mm, whichever is greater). In addition, it was suggested that the test should specify that the force be applied to cell faces that are perpendicular to the terminal face, in the case of prismatic cells. Finally, since large cells may require very high, and, therefore, unrealistic forces to be applied in order to induce an internal short circuit through cell deformation, it was also suggested that the maximum force required to be applied in the test be limited to 10 kN (one metric ton). These comments have been incorporated into the proposed amendments to Test T.4.

9. Test T.5.

9.1 Comments on document ST/SG/AC.10/C.3/1997/83 suggested that certain modifications were necessary to the shock and low capacity cell test provisions in Test T.5 to properly take account of the practical aspects of testing and shipping large cells and batteries. With regard to the shock test provisions, the same suggestions were made as were described above in relation to the shock test provisions of Test T.2. With regard to the low capacity cell test provisions, it was noted that for large batteries it may not always be possible (for reasons such as are outlined in 7.1, above) to achieve a current draw corresponding to the maximum discharge rate specified by the manufacturer when employing the testing procedure prescribed in 38.3.4.5.3.3. In such cases, it was suggested to limit the required current draw to the maximum attainable under the prescribed test procedure at the ambient temperature at which the test is performed. These comments have been incorporated into the proposed amendments to Test T.5.

10. Test T.6.

10.1 No written comments were received regarding the amendments proposed in document ST/SG/AC.10/C.3/1997/83 relative to Test T.6. However, in subsequent discussions between experts regarding the maximum discharge current required to be achieved during the forced discharge testing of large cells, it was again noted that it may not always be possible (for reasons

such as are outlined in 7.1, above) to achieve a current draw corresponding to the maximum current specified by the manufacturer when employing the testing procedure prescribed in 38.3.4.6.3. It was suggested that in such cases the current draw required to be achieved be limited to the maximum attainable under the prescribed test procedure at the ambient temperature at which the test is performed. This comment has been incorporated into the proposed amendments to test T.6.

**Proposals**

11. In light of the foregoing, the following amendments to the UN Recommendations are proposed:

a) In Special Provision 230:

(i) Add a new first sentence to read:

"This entry applies to cells and batteries containing lithium in any form, including lithium polymer and lithium ion cells and batteries."

(ii) Delete (b) and (c), and redesignate (d), (e), (f) and (g) as (b), (c), (d) and (e), respectively;

(iii) Revise new (d) [i.e., the current (f)] to read:

"each battery containing cells or series of cells connected in parallel is equipped with effective means as necessary to prevent dangerous reverse current flow (e.g., diodes, fuses, etc.);"

b) In Special Provision 240, replace the words "or sodium batteries" after "powered by wet batteries" by the words "sodium batteries, or lithium batteries".

c) Add a new Special Provision 28A to UN 3090 to read:

28A New, uncycled and uncharged lithium ion cells and batteries are not subject to these regulations if:

a) The electrolyte does not meet the definition of any class or division in these regulations; or

b) If the electrolyte meets the definition of a hazard class or division in these regulations, the electrolyte will not flow from a ruptured or cracked case and there is no free liquid to flow.

12. In addition, the following amendments are proposed to the Manual of Tests and Criteria:

a) In 38.3.3.2, add the following new definitions in appropriate alphabetical sequence:

"*Large battery* means a battery in which the aggregate lithium content of all anodes, when fully charged, is more than 500 g. (For an explanation of "lithium content", see Special Provision 188.)"

"*Large cell* means a cell in which the lithium content of the anode, when fully charged, is more than 12 g."

"*Small battery* means a battery composed of small cells, and in which the aggregate lithium content of all cell anodes, when fully charged, is not more than 500 g."

"*Small cell* means a cell in which the lithium content of the anode, when fully charged, is not more than 12 g."

c) In 38.3.4.1 ("Test T.1"):

1) Revise the introductory text in 38.3.4.1.2.2 to read:

"For small cells and small batteries, the number and condition of cells and batteries to be tested are as follows:" [(a) to (f) unchanged]

2) Add a new 38.3.4.1.2.3 to read:

"For large cells and large batteries, the number and condition of cells and batteries to be tested are as follows:

(a) Only when cells are to be transported individually --

(i) Ten cells which should be tested, at first cycle, in both fully charged and fully discharged states; and

(ii) Ten cells which should be tested after deep cycling a minimum of 50 times, in both fully charged and fully discharged states.

(b) Four batteries, which should be tested, at first cycle, in both fully charged and fully discharged states.

(c) Four batteries, which should be tested after deep cycling a minimum of 50 times, in both fully charged state and fully discharged states."

3) In 38.3.4.1.3.2, replace the time period "5 minutes" by the time period "10 minutes" in the second sentence.

d) In 38.3.4.2 ("Test T.2"):

1) In 38.3.4.2.2.1, revise the second sentence to read:

"The shock test apparatus should be constructed to give the minimum accelerations required by 38.2.3.2.3.2 for the size of cell or battery being tested, e.g., apparatus to IEC 68-2-27."

2) Revise the introductory text in 38.3.4.2.2.2 to read:

"For small cells and small batteries, the number and condition of cells and batteries to be tested are as follows:" [(a) to (f) unchanged]

3) Add a new 38.3.4.2.2.3 to read:

"For large cells and large batteries, the number and condition of cells and batteries to be tested are as follows:

(a) Only when cells are to be transported individually --

(i) Ten cells which should be tested, at first cycle, in both fully charged and fully discharged states; and

(ii) Ten cells which should be tested after deep cycling a minimum of 50 times, in both fully charged and fully discharged states.

(b) Four batteries, which should be tested, at first cycle, in both fully charged and fully discharged states.

(c) Four batteries, which should be tested after deep cycling a minimum of 50 times, in both fully charged state and fully discharged states."

4) In 38.3.4.2.3.2, replace the last two sentences of the current text with the following:

"In each case, the cell or battery is accelerated in such a manner that:

(a) For small cells and small batteries, during the first three milliseconds the minimum average acceleration is 75 times the local acceleration due to gravity, and the peak acceleration is between 125 and 175 times the local acceleration of gravity; or

(b) For large cells and large batteries, a peak acceleration of not

less than 50 times the local acceleration of gravity is achieved over a maximum duration of 11 milliseconds."

e) In 38.3.4.3 ("Test T.3"):

1) In 38.3.4.3.2.1, revise the second sentence to read:

"The shock test apparatus should be constructed to give the minimum accelerations required by 38.2.3.2.3.2 for the size of cell or battery being tested, e.g., apparatus to IEC 68-2-27."

2) Revise 38.3.4.3.2.2 to read:

"For small cells and small batteries, the number and condition of cells and batteries to be tested are as follows:" [38.3.4.3.2.2.1 to 38.3.4.3.2.2.3 unchanged]

3) Add a new 38.3.4.3.2.3 to read:

"For large cells and large batteries, tests need not be performed on batteries, and the number and condition of cells to be tested are as follows:

(a) Ten cells which should be tested, at first cycle, in the fully charged state; and

(b) Ten cells which should be tested after deep cycling a minimum of 50 times, in the fully charged state."

4) In 38.3.4.3.3.2, replace the last two sentences of the current text with the following:

"In each case, the cell or battery is accelerated in such a manner that:

(a) For small cells and small batteries, during the first three milliseconds the minimum average acceleration is 75 times the local acceleration due to gravity, and the peak acceleration is between 125 and 175 times the local acceleration of gravity; or

(b) For large cells, a peak acceleration of not less than 50 times the local acceleration of gravity is achieved over a maximum duration of 11 milliseconds."

5) In 38.3.4.3.3.3, amend the fifth sentence (by adding the word "continuous" after the word "maximum"), and insert a new sixth sentence, so that the fifth and sixth sentences read:

"Where the cell or battery contains no protective devices, the resistive load is such that the average current draw is the same as the maximum continuous discharge current specified by the manufacturer. When for large cells this average current draw cannot be achieved employing this test procedure, the current draw required is the maximum current attainable according to this test procedure at the ambient temperature at which the test is performed."

f) In 38.3.4.4 ("Test T.4"):

1) In 38.3.4.4.2.1, replace the words "a 6 mm (diameter) rod" with the words "a rod with a diameter of at least 50% of the smallest cell overall dimension, or 6 mm, whichever is greater".

2) Transfer the first two sentences of 38.3.4.4.2.2 to the end of the "Introduction" section, (i.e., 38.3.4.4.1), and revise the third sentence to read:

"For small cells, the number and conditions of cells to be tested are as follows:" [(a) to (d) unchanged]

3) Add a new 38.3.4.4.2.3 to read (reminder of paragraphs to be renumbered):

"For large cells, ten cells should be tested, at first cycle, in the fully charged state."

4) Revise 38.3.4.4.3 to read:

"Each cell is deformed until the open circuit voltage drops abruptly or is reduced to at least one third, or until a maximum force of 10 kN is applied. The deformation is effected by placing the rod between one jaw of the clamping device and the cell and applying force. In the case of prismatic cells, the force is to be applied to each face that is perpendicular to the terminal face. The applied force is removed at the point at which the cell voltage drops, or when the maximum 10 kN force is achieved, whichever occurs first.

g) In 38.3.4.5 ("Test T.5"):

1) In 38.3.4.5.2.1, revise the second sentence to read:

"The shock test apparatus should be constructed to give the minimum accelerations required by 38.2.3.5.3.2 for the size of cell or battery being tested, e.g., apparatus to IEC 68-2-27."

2) Revise the introductory text in 38.3.4.5.2.2 to read:

"For small cells and small batteries, the number and condition of cells and batteries to be tested are as follows:" [(a) and (b) unchanged]

3) Add a new 38.3.4.5.2.3 to read:

"For large cells and large batteries, batteries should be constructed with uncycled cells except for one in each series string which is deep cycled a minimum of 50 times, and then brought to a 60 % state of charge. Four batteries are tested at first cycle in the fully charged state."

4) In 38.3.4.2.3.2, replace the last two sentences of the current text with the following:

"In each case, the cell or battery is accelerated in such a manner that:

(a) For small cells and small batteries, during the first three milliseconds the minimum average acceleration is 75 times the local acceleration due to gravity, and the peak acceleration is between 125 and 175 times the local acceleration of gravity; or

(b) For large cells and large batteries, a peak acceleration of not less than 50 times the local acceleration of gravity is achieved over a maximum duration of 11 milliseconds."

5) In 38.3.4.5.3.3, insert a new penultimate sentence to read:

"When for large batteries this average current draw cannot be achieved employing this test procedure, the current draw required is the maximum current attainable according to this test procedure at the ambient temperature at which the test is performed."

h) In 38.3.4.6 ("Test T.6"):

1) Revise 38.3.4.6.2.2 to read:

"For small cells and small batteries, the number and condition of cells and batteries to be tested are as follows:" [38.3.4.6.2.2.1 to 38.3.4.6.2.2.3 unchanged]

2) Add a new 38.3.4.6.2.3 to read:

"For large cells and large batteries, tests need not be performed on batteries, and need only be performed on component cells when the battery voltage does not exceed 12 volts. When required to be tested, the number and condition of cells to be tested are as follows:

(a) Ten cells which should be tested, at first cycle, in the fully discharged state.

(b) Ten cells which should be tested, after deep cycling a minimum of 50 times, in the fully discharged state.

3) In 38.3.4.6.3, insert a new sentence following the sixth sentence (i.e., the sentence beginning "Where the cell or battery contains no protective devices...") to read:

"When for large cells this average current draw cannot be achieved employing this test procedure, the current draw required is the maximum current attainable according to this test procedure at the ambient temperature at which the test is performed."

i) In 38.3.4.7 ("Series T test criteria and method of assessing results"), 38.3.4.7.2 would be amended by replacing the words "subject to the mass requirements in Special Provision 230" with the words "not excepted from these Recommendations according to 38.3.4.7.1."

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# MISCELLANEOUS DRAFT AMENDMENTS TO THE MODEL REGULATIONS ON THE TRANSPORT OF DANGEROUS GOODS

## Other draft amendments

## Listing and classification
## Lithium batteries: Special Provision 188

Transmitted by the experts from France, Germany and the United States of America

## Background

1. In document ST/SG/AC.10/C.3/1997/83, the expert from the United States proposed to amend certain mass limitations applicable to lithium cells and batteries in such a way that these limits would apply to the aggregate "lithium content" of the negative electrodes of the cells or batteries, rather than to the aggregate mass of "lithium or lithium alloy" in the cells or batteries (as is provided in the current Recommendations). As stated in that document, similar terminology should be employed in the text of Special Provision 188, in which mass limitations are also specified in terms of mass of "lithium or lithium alloy". Therefore, this document proposes that Special Provision 188 be amended accordingly.

2. Further information with regard to the concept underlying these proposals is presented in section 3 of document ST/SG/AC.10/C.3/1998/??.

**Proposals**

3. The following amendments are proposed to Special Provision 188:

(a) Amend (a) to read:

> For a cell with a liquid cathode, the lithium content of the anode, when fully charged, is not more than 0.5 g, and for a cell with a solid cathode, the lithium content of the anode, when fully charged, is not more than 1 g;

(b) Amend (b) to read:

> For a battery with liquid cathodes, the aggregate lithium content of the anodes, when fully charged, is not more than 1g, and for a battery with solid cathodes, the aggregate lithium content of the anodes, when fully charged, is not more than 2 g;

(c) Amend beginning of (f) to read:

> If, when fully charged, the aggregate lithium content of the anodes in a liquid cathode battery is more than 0.5 g, or of the aggregate lithium content of the anodes in a solid cathode battery is more than 1 g, it does not contain a liquid or gas...[remainder unchanged]

(d) Amend (g) to read:

> The lithium content of the anode of each cell, when fully charged, is not more than 5 g;

(e) Amend (h) to read:

> The aggregate lithium content of the anodes of each battery, when fully charged, is not more than 25 g;

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# MISCELLANEOUS DRAFT AMENDMENTS TO THE MODEL REGULATIONS ON THE TRANSPORT OF DANGEROUS GOODS

## Toxic by inhalation substances
## Consignment requirements

Transmitted by the Expert from the United States of America

## Introduction

1. During the thirteenth and fourteenth sessions, the Sub-Committee considered the issue of amending the Model Regulation to include special requirements for substances that are toxic by inhalation (TIH substances). This topic was discussed on the basis of ST/SG/AC.10/C.3/1997/20 and ST/SG/AC.10/C.3/1997/81 which contained specific proposals for new hazard communication requirements for TIH substances. The intention of proposals on TIH substances is to improve the hazard communication of these substances for purposes of transport acceptance and emergency services personnel, and to improve the packaging of such materials to reduce the likelihood of release in transport. The previous papers provide the justification for why the expert from the United States considers it necessary to adopt additional requirements for this group of substances. To facilitate discussion of this topic, the proposals in the two previous papers are being resubmitted in four separate papers for the fifteenth session. The purpose of this paper is to recommend specific requirements for improving hazard communication with respect to these substances.

2. The proposals are similar to those made previously in ST/SG/AC.10/C.3/1997/81; however, some adjustments to the proposals in ST/SG/AC.10/C.3/1997/81 were made on the basis of the indicative votes held during the fourteenth session.

**Definition of TIH substances**

3. As now discussed in ST/SG/AC.10/C.3/1998/29 only inhalation toxicity substances of Division 6.1 and gases of Division 2.3 (label proposal only) would be subject to the hazard communication requirements proposed.

**NOS Proper shipping names**

4. It is proposed that new NOS entries be adopted to better distinguish between Division 6.1 TIH substances that are transported under NOS proper shipping names which meet the inhalation toxicity criteria and those that do not meet the criteria. It is proposed that this distinction be made through the inclusion of the words "Toxic by Inhalation" in each new shipping name. The following new entries are proposed:

| (2) | (3) | (4) | (5) | (6) | (7) |
|---|---|---|---|---|---|
| TOXIC BY INHALATION LIQUID, N.O.S. | 6.1 | | I | 109<br>274<br>xxx | NONE |
| TOXIC BY INHALATION LIQUID, FLAMMABLE, N.O.S. | 6.1 | 3 | I | 109<br>274<br>xxx | NONE |
| TOXIC BY INHALATION LIQUID, WATER-REACTIVE, N.O.S. | 6.1 | 4.3 | I | 109<br>274<br>xxx | NONE |
| TOXIC BY INHALATION LIQUID, OXIDIZING, N.O.S. | 6.1 | 5.1 | I | 109<br>274<br>xxx | NONE |
| TOXIC BY INHALATION LIQUID, CORROSIVE, N.O.S. | 6.1 | 8 | I | 109<br>274<br>xxx | NONE |

Each of these entries should have the following special provision indicated in column 6 of the Dangerous Goods list:

> "XXX This entry shall only be used for Division 6.1 substances that meet the inhalation toxicity criteria for Packing Group I described in 2.6.2.2.4.3."

Proposed packaging and portable tank requirements are provided in ST/SG/AC.10/C.3/1998/27 and -28.

5. To prevent existing toxic liquid NOS entries not meeting the inhalation toxicity criteria a special provision indicating that those entries should not be used if the substance meets the TIH criteria should be placed against each such NOS entry which would no longer be appropriate for TIH substances. This special provision should also be placed against several chemical specific entries including UN 1614, 1744, and 3294. The new special provision should read:

> "YYY This entry shall not be used for Division 6.1 substances that meet the inhalation toxicity criteria for Packing Group I described in 2.6.2.2.4.3."

This special provision should appear in column 6 of the Dangerous Goods List against the following entries:

1583,1614, 2810, 2927, 2929, 3122, 3123,3275, 3276,3278,3279,3280,3281,3287, 3289,and 3294.

**Labelling and placarding**

6. To emergency responders, labels and placards usually provide the first sign that a substance involved in an incident is dangerous and provide information on the nature of the danger posed. For TIH substances, given their ability to evaporate and disperse through the atmosphere, it is particularly important that the responder is able to recognize the type of substance involved at a considerable distance from the sight of the incident.

7. Division 6.1 includes substances that are toxic by oral, dermal and inhalation routes of exposure. The number of TIH substances included in Division 6.1 is small relative to the number of substances included in Division 6.1. Under the current system, not being able to distinguish TIH substances from other Division 6.1 substances could lead to overly cautious and expensive precautionary measures being taken in the event of an incident involving a Division 6.1 substance that does not meet the TIH criteria. Conversely frequent exposure to other Division 6.1 substances could lead to complacency among response personnel resulting in them being insufficiently cautious in the event of an incident involving a TIH substance.

8. The existing Division 2.3 and 6.1 labels and placards are not readily visible from a distance. Further, the expert from the United States considers that a label and placard distinct from the existing Division 6.1 label is necessary to effectively communicate the risk of TIH substances to emergency response personnel. Because Division 2.3 and Division 6.1 substances pose the same type of inhalation hazard risk, it is also proposed that the same label and placard be used for both Division 2.3 and Division 6.1 substances. Proposed labels for TIH liquids and gases are shown in Annex 1. While the proposed labels do not pictorially convey the toxic by inhalation hazard, they are visible from long distances and they are clearly distinct from the label used for other toxic substances. Tests have shown that the label is discernable at a distance of at least 100 metres. As such, they will enable *trained* emergency services personnel to recognize the toxic inhalation hazard the labels and placards are intended to convey.

9. It is proposed that the Class 2.3 label shown in Annex 1 replace label No. 2.3 in 5.2.2.2.2.1 and that the existing No.6.1 label would be redescribed as:

(No. 6.1A)
Division 6.1
Toxic substances other than Packing Group I toxic by inhalation substances

The Division 6.1 label shown in Annex 1 would be added to 5.2.2.2.2.1 as an additional label with the following description:

(No. 6.1B)
Division 6.1
Packing Group I toxic by inhalation substances

**Documentation**

10. In the case of substances transported under new NOS descriptions, the fact that a substance is a TIH substance will be clear from the proper shipping name that is used. In the case of Division 2.3 gases, it will be clear from the 2.3 Division indicated in the basic description. However, for substances transported under specific shipping names, no information currently required to be provided on the shipping paper conveys the information that the substance is a TIH substance. It is proposed that on shipping papers listing TIH substances under a specific chemical proper shipping name that the words "Toxic by Inhalation" be required to be placed on the shipping paper immediately after the basic description.

11. It is proposed that a new paragraph 5.4.1.1.6 be added (existing 5.4.1.1.6 and subsequent paragraphs renumbered) as follows:

"5.4.1.1.6 *Special provision for Division 6.1 toxic by inhalation substances*

For Division 6.1 substances that meet the vapour inhalation toxicity criteria for Packing Group I (see 2.6.2.2.4.3) that are described on the transport document by a proper shipping name that does not convey that the substance is toxic by inhalation, the words "Toxic by Inhalation" shall be placed immediately following the basic description required by 5.4.1.1.1."

**Identification of substances meeting the inhalation criteria for Division 6.1, Packing group I**

12. To identify those named substances to which the proposed new Division 6.1 label, and the proposed transport document provision would apply, it is proposed that a new special provision be added in column 6 of the Dangerous Goods List as follows:

> "ZZZ This substance is considered to meet the inhalation toxicity criteria of Division 6.1, Packing Group I. The model No. 6.1B label and placard shall be used and the substance shall be described on the transport document in accordance with 5.4.1.1.6."

Note: For the NOS descriptions, special provision XXX could be modified to include the following: "Model No. 6.1B labels and placards shall be used."

13. List of substances which the expert from the United States considers as meeting these criteria are provided in ST/SG/AC.10/1998/29. It is proposed that special provision ZZZ be placed against each of these substances.

**ANNEX 1**

**LABEL**

6

**Annex**

List of substances in the United Nations' Dangerous Goods List
known to be toxic by inhalation

| *LIST OF GROUP IA SUBSTANCES* | | | | | | | |
|---|---|---|---|---|---|---|---|
| ***UN NO.*** | ***SUBSTANCE*** | ***LC50 (ppm)*** | ***LCLo (ppm)*** | ***NOTE*** | ***V (20° C) (ppm)*** | ***NOTE*** | ***RTECS***** |
| UN 2484 | tert-Butyl isocyanate | 22 | – | A | 19700 | | NQ8300 |
| UN 1745 | Bromine pentafluoride | – | 50 | eS | 453000 | | EF9350 |
| UN 1744 | Bromine | 113 | – | R*[illegible] | 237000 | | EF9100 |
| UN 1092 | Acrolein, inhibited | 25 | – | D | 289000 | | AS1050 |
| UN 1834 | Sulfuryl chloride | 131 | – | C | 142000 | | WT4870 |
| UN 2482 | n-Propyl isocyanate | 44 | – | A | 69700 | | NR0190 |
| UN 1380 | Pentaborane | 12 | – | R* | 225000 | | RY8925 |
| UN 1259 | Nickel carbonyl | 18 | – | R* | 422000 | | QR6300 |
| UN 1251 | Methyl vinyl ketone, stabilized | 5 | – | C* | 93400 | | EM9800 |
| UN 2480 | Methyl isocyanate | 22 | – | A* | 458000 | | NQ9450 |
| UN 1244 | Methylhydrazine | 68 | – | R* | 50300 | | MV5600 |
| UN 1185 | Ethyleneimine, inhibited | 76 | – | R* | 217000 | | KX5075 |
| UN 2481 | Ethyl isocyanate | – | – | 14 | – | | NQ8825 |
| UN 1239 | Methyl chloromethyl ether | 160 | – | R* | 210000 | | KN6650 |
| UN 1238 | Methyl chloroformate | 88 | – | R | 135000 | | PG3675 |
| UN 2605 | Methoxymethyl isocyanate | – | – | 14 | – | | NQ9240 |
| UN 1051 | Hydrogen cyanide, stabilized | 40 | – | R* | 842000 | | MW6825 |
| UN 2483 | Isopropyl isocyanate | – | – | 14 | – | | NQ9230 |
| UN 2486 | Isobutyl isocyanate | – | – | 14 | – | | NQ9208 |
| UN 1994 | Iron pentacarbonyl | 6 | – | R? | 30300 | | NO4900 |

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Sub-Committee of Experts on the
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# MISCELLANEOUS DRAFT AMENDMENTS TO THE MODEL REGULATIONS ON THE TRANSPORT OF DANGEROUS GOODS

## Toxic by inhalation substances
## Packaging requirements

Transmitted by the Expert from the United States of America

## Introduction

1. In document ST/SG/AC.10/C.3/1997/20 (USA) submitted to the thirteenth session of the Sub-Committee possible packing instructions for TIH substances of Group IA (substances with an inhalation toxicity of 250 ml/m$^3$ or less and $V \geq 500LC_{50}$) and IB (substances with an inhalation toxicity of less than or equal to 1000 ml/m$^3$ and $V \geq 10LC_{50}$) were identified. Some comments were received and the expert from the United States agreed to consider them in the development of further packaging proposals for TIH substances. The purpose of this paper is to propose TIH packaging instructions.

2. As noted in ST/SG/AC.10/C.3/1997/20 in addition to US regulations, other regulatory systems such as IMO and ADR/RID also include packaging provisions for selected TIH substances. In all likelihood, similar to the experience in the United States, these requirements were adopted on the basis of industry proposals when there was a need to transport these particular substances. The types of packagings authorized can be characterized as including:

- steel cylinders,
- special combination packagings with specifically prescribed inner packaging and requirements for cushioning material, and
- special metal drums with in some cases able to withstand high test pressures (5 to 10 bar).

3. The expert from the United States in response to comments received at the thirteenth session considered proposing packaging provisions which were strictly performance oriented. In particular a puncture test simulating a fork lift tine striking the packaging was experimented with. The test showed significantly better puncture resistance in the case of existing packagings authorized for use for TIH substances under US regulations. However, under the time constraint of including packaging provisions by December 1998, it does not appear that there is sufficient time to fully develop puncture test criteria for such packagings.

**Proposed packing instructions**

4. There is some commonality among existing packaging provisions currently applied to TIH substances in various regulations. In all cases, packing instructions prescribed for TIH substances are intended to decrease the risk that substances are released in transportation incidents. While the existing UN performance tests provide an acceptable degree of protection in the case of most dangerous goods, the packagings currently prescribed for TIH substances imply a desire to enhance the survivability of TIH packagings. Furthermore, as the risk of a significant release varies with the size of the packaging, the level of severity of the packaging requirements varies according to the quantity of substance in the packaging.

5. In reviewing the various packagings provisions currently prescribed for TIH substances, the expert from the United States concludes that all substances can be dealt with under two generic packing instructions.

6. The basic philosophy behind the packagings proposed in the packing instructions attached as Annex 1 is to allow the substance to be transported in

- an extremely robust packaging ( i.e, a gas cylinder);
- in single packagings overpacked with an additional UN tested packaging, with each packaging qualified to retain the substance;
- in combination packagings that consist of three packagings; and
- for Group IB substances in high integrity single packagings for "exclusive use shipments" (shipments going from a consignor to a single consignee without intermediate transfer) in a freight container or transport unit.

7. The concept of the packagings proposed is not new. Other substances of high danger substances covered by the Model Regulation are already required to be transported in similar packagings (e.g., certain explosives and infectious substances).

8. It is proposed that the packing instruction P004 be adopted for Group IA TIH substances and that packing instruction P005s be adopted for Group IB TIH substances.

| P004 | PACKING INSTRUCTION | P004 |
|---|---|---|

The following packagings are authorized:

(a) Gas cylinders conforming to the construction, testing and filling requirements approved by the competent authority. Each cylinder with a wall thickness less than 3 mm must be overpacked in a strong outer packaging and secured or cushioned so as to prevent significant movement within the outer packaging during normal conditions of transport.

(b) 1A1, 1B1, and 1H1 drums or 6HA1 composite packagings with a capacity not exceeding 220 litres which are overpacked in 1A2 or 1H2 drums are authorized. The overpacked package shall conform to the following requirements:

(1) the package shall be of a design type meeting the requirements prescribed in Chapter 6.1 at the PG I performance level for liquids except that:

(i) the hydrostatic pressure test shall be carried out at a pressure of at least the greater of two times the vapor pressure of the substance to be transported at 55°C or 300 kPa; and

(ii) the design and production leakproofness tests shall be carried out at a test pressure of at least the greater of two times the vapor pressure of the substance to be transported at 55°C or 0.30 bar.

(2) closures shall be of a screw cap type that are :

(i) physically held in place by any means capable of preventing back-off or loosening of the closure by impact or vibration during transport; and

(ii) provided with a cap seal that is capable of withstanding an internal pressure of at least 100 kPa.

(3) be so packed inside the outer drum overpack using inert absorbent and cushioning material so that no outside surface of the overpacked package is less than 5 cm from any inside surface of the overpacking drum.

The outer drum shall:

(i) conform to the performance test requirements for solids at the Packing Group I performance level; and
(ii) shall withstand a hydrostatic pressure test in accordance with Chapter 6.1 at a pressure of at least 100 kPa.

(c) In combination packagings, consisting of an inner packaging system and one of the following outer packagings:
Drums: 1A2, 1B2, 1D, 1G and 1H2
Jerricans: 3A2, 3H2
Boxes: 4A, 4B, 4C1, 4C2, 4D, 4F, 4G, 4H1 and 4H2

(1) The inner packaging system shall consist of impact-resistant glass, plastic or metal receptacles cushioned with an inert absorbent material inside a leakproof packaging of metal or plastic. The capacity of each inner receptacle shall not exceed 4 litres. The closure of each inner receptacle shall be physically held in place by any means capable of preventing back-off or loosening of the closure by impact or vibration during transport. The inner packaging system shall conform to the performance test requirements of Chapter 6.1 at the PG I performance level without the benefit of the outer packaging.
(2) The outer packaging shall also conform to the performance test requirements of Chapter 6.1 at the PG I performance level as a single packaging suitable for solids.
(3) The amount of liquid contained within the outer packaging may not exceed 16 litres.

*This packing instruction applies to Group IA (substances with an inhalation toxicity of 250 ml/m³ or less and V ≥ 500LC$_{50}$)*

**P005** **PACKING INSTRUCTION** **P005**

The following packagings are authorized:
(a) Packagings that are authorized in packing instruction P004.
(b) 1A1, 1B1 and 1H1 drums or 6HA1 composite packagings with a capacity not exceeding 220 litres are authorized as single packagings subject to the following requirements and conditions:

(1) packagings shall be of a design type meeting the requirements prescribed in Chapter 6.1 at the PG I performance level for liquids except that:

(i) the hydrostatic pressure test shall be carried out at a pressure of at least the greater of two times the vapor pressure of the substance to be transported at 55°C or 300 kPa; and

(ii) the design and production leakproofness tests shall be carried out at a test pressure of at least the greater of two times the vapor pressure of the substance to be transported at 55°C or 0.30 bar.

(2) The minimum thickness of each package shall be at least:

| PACKAGING TYPE | | MINIMUM THICKNESS FOR EACH CAPACITY RANGE | | |
|---|---|---|---|---|
| | | CAPACITY <= 30 l | 30 l < CAPACITY <= 120 l | 120 l < CAPACITY <= 220 l |
| 1A1 | | 0.7 mm | 1.1 mm | 1.4 mm |
| 1B1 | | 2.8 mm | 3.9 mm | 4.7 mm |
| 1H1 | | 2.0 mm | 3.2 mm | 3.2 mm |
| 6HA1 | INNER RECEPTACLE | 1.6 mm | 1.6 mm | 1.6 mm |
| | OUTER RECEPTACLE | 0.7 mm | 1.0 mm | 1.1 mm |

(3) closures shall be of a screw cap type that are :

(i) physically held in place by any means capable of preventing back-off or loosening of the closure by impact or vibration during transport; and

(ii) provided with a cap seal that is capable of withstanding an internal pressure of at least 100 kPa.

(4) packages are transported in a transport unit loaded, blocked, braced and sealed by the consignor;

(5) Packages are not be stacked within the transport unit;

(6) the consignment is from one origin to one destination only without any intermediate pickup or delivery;

*This packing instruction applies Group IB (substances with an inhalation toxicity of less than or equal to 1000 ml/m³ and $V \geq 10LC_{50}$ that do not meet Group IA criteria )*